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Accelerated light-induced degradation for detecting copper contamination in *p*-type silicon

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Copper is a harmful metal impurity that significantly impacts the performance of silicon-based devices if present in active regions. In this contribution, we propose a fast method consisting of simultaneous illumination and annealing for the detection of copper contamination in p-type silicon. Our results show that, within minutes, such method is capable of producing a significant reduction of the minority carrier lifetime. A spatial distribution map of copper contamination can then be obtained through the lifetime values measured before and after degradation. In order to separate the effect of the light-activated copper defects from the other metastable complexes in low resistivity Cz-silicon, we carried out a dark anneal at 200 °C, which is known to fully recover the boron-oxygen defect. Similar to the boron-oxygen behavior, we show that the dark anneal also recovers the copper defects. However, the recovery is only partial and it can be used to identify the possible presence of copper contamination. © *2015 AIP Publishing LLC*.
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Copper contamination is a serious issue in both solar-cell[1] and semiconductor technologies[2] because of its detrimental effect on minority carrier lifetime and diffusion length. Due to the high copper diffusivity and solubility,[3] the avoidance of copper contamination is rather challenging during the growth of silicon ingots and the subsequent solar-cell fabrication steps. Furthermore, additional copper contamination may result from recently introduced copper contacts in both integrated circuits and solar cells, despite the use of specific copper diffusion barriers. The presence of copper contamination in silicon can be detected by quantitative methods, such as transient ion drift (TID)[4] and total reflection x-ray fluorescence (TXRF).[5] However, the former method requires immediate measurements after contact formation, while the latter is limited to measuring only near-surface concentrations. Furthermore, both TID and TXRF methods are destructive and time-consuming methods.[6]

Recently, copper has been observed to reduce the minority carrier lifetime during prolonged annealing in the dark or illumination at room temperature. The activation of recombination-active defects during light soaking is commonly referred to as copper-related light-induced degradation (Cu-LID). The Cu-LID has been confirmed to originate from bulk recombination,[5] which is proposed to be caused by copper precipitation[7] or substitutional copper release through copper complex dissociation during illumination.[8,9] The formed defects have been found to be stable at 200 °C in wafers with initial interstitial copper concentration of $10^{14}\,\mathrm{cm}^{-3}$.[10]

In addition to copper defects, the involvement of boron and oxygen in the formation of a metastable recombination-active defect (BO-LID) has been extensively reported as the major cause of degradation in low-resistivity boron-doped Czochralski (Cz) silicon.[11] BO-LID is typically observed as a two-exponential lifetime decay within 24 h of illumination, which is fully recoverable at 200 °C.[12] The lifetime decrease and the normalized defect density can easily be measured for both BO-LID and Cu-LID by contactless and non-destructive characterization methods, such as quasi-steady-state photoconductance (QSSPC),[13] microwave photoconductive decay (μ-PCD),[14] and surface photovoltage (SPV).[15] Since the normalized Cu-LID defect has been found proportional to the initial interstitial copper concentration,[7] lifetime measurements before and after degradation provide an estimate for the interstitial copper concentration. The main drawback of this copper-detection technique is the long illumination time needed for a saturation of the observed lifetime decay.

In order to decrease the BO-LID detection time, a new method called accelerated light-induced degradation (ALID) has been recently developed.[16] The method relies on illumination at elevated temperatures (120 °C), achieving full degradation within only 10 min.[17] In this letter, our goal is to deepen the understanding of the formation kinetics of light-activated copper defects by analyzing the impact of the ALID method on Cu-LID. Second, we also want to determine whether this ALID method can be employed for rapidly detecting the presence of copper contamination in silicon.

The experiments were performed on ⟨100⟩ oriented, 4-in., boron-doped, electronic-grade Cz- silicon with resistivity of 3.4–3.9 Ω cm, thickness of ∼380 μm, and an oxygen concentration higher than 14.5 ppma. After standard RCA cleanings, the wafers were passivated through the growth of a 15 nm thick thermal oxide layer, formed during 40 min of dry oxidation at 900 °C, followed by annealing in nitrogen at the same temperature for 20 min. A contamination solution containing 1 ppm of copper sulfate solution was then spinned onto the front surface of each wafer, which quickly turned into interstitial copper bulk contamination during annealing in nitrogen atmosphere at 800 °C. Next, an external corona

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charge ($+0.3\,\mu C/cm^2$) was deposited onto both sides of the wafer, in order to prevent copper out-diffusion[6] and reduce the surface minority carrier recombination through the creation of an inversion layer near the surface.

Before illumination, the samples were annealed in the dark at 200 °C for 2 min to deactivate any metastable active complex formed during sample preparation. Since annealing reduces the surface corona charge, $+0.06\,\mu C/cm^2$ was added onto each side of the wafer.[10] The samples were then divided into two separate batches that underwent different degradation treatments. The first batch went through illumination at room temperature for 24 h under a 0.5 Sun Xenon lamp, i.e., a RT-LID treatment. The second batch of wafers was subjected to the ALID procedure, consisting of illumination with the same Xenon light source and simultaneous heating at the temperature of 120 °C.[17] During the ALID and the RT-LID treatments, the effective minority carrier lifetime was monitored with QSSPC measurements at the injection level of $\Delta n = 0.1 \cdot N_{dop}$, ensuring that the measured lifetime is dominated by Schockley-Read-Hall recombination.

Figure 1 presents the minority carrier lifetime measured in identical Cu-contaminated wafers during ALID and RT-LID. The ALID method clearly accelerates the formation kinetics of light-activated copper defects compared with RT-LID, which is in analogy with previous ALID data reported for the B-O complex. This result hence raises the question whether the possible effect of copper has been ignored in previous publications on ALID.[16]

Figure 1 also shows that during ALID a large portion of the lifetime decay takes place during the first few minutes, suggesting that the degradation kinetics are initially very fast and progressively slow down until a saturation is reached. By comparing the lifetime values measured during ALID and RT-LID after identical degradation time steps, it becomes evident that ALID results in almost complete lifetime saturation within 1 h, whereas RT-LID requires almost a whole day to reach similar degradation. Note that the Cu-related degradation rate depends on the annealing temperature,[10] light intensity,[9,14] and impurity concentration,[7] enabling probably even faster lifetime saturation at higher temperatures, illumination intensities, or copper concentrations.

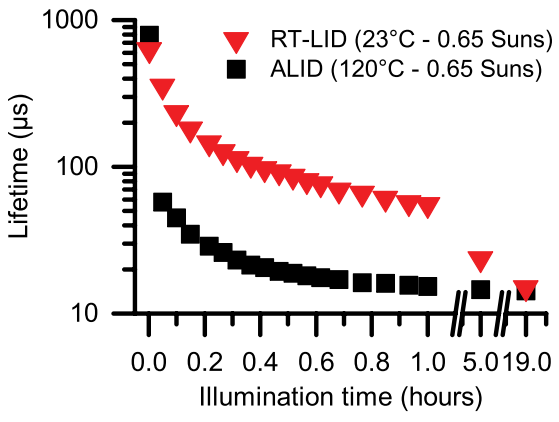

FIG. 1. Minority carrier lifetime as a function of the illumination time measured in identical Cu-contaminated Cz-wafers during ALID and conventional room-temperature degradation (RT-LID). The lifetime was measured with QSSPC at the injection level of $3 \times 10^{14}\,cm^{-3}$.

The strong impact of 120 °C annealing on the degradation kinetics can be explained by the higher copper diffusivity at increasing temperatures.[18,19] Since copper is known to form unstable CuB complexes that constantly pair and dissociate even at room temperature, the diffusivity of interstitial copper is further increased by the complete dissociation of Cu-B pairs at 120 °C in 3.4–3.9 Ω cm silicon.[20] This result is in accordance with recent studies proving that Cu-LID is a bulk phenomenon[5] limited by copper diffusion.[10]

In order to further study the applicability of ALID for measuring copper in silicon, we intentionally contaminated only a small portion of the wafer by depositing a 20 ppb copper sulfate solution droplet ($\approx 7\,cm^2$) on the wafer front surface. This was followed by the same in-diffusion anneal and ALID/RT-LID treatments as previously described. The minority carrier diffusion length was then analyzed in both clean and intentionally contaminated areas with the SPV technique, which allows a detailed minority carrier diffusion length mapping at low injection level (excess carrier concentration of $\sim 10^{12}\,cm^{-3}$). Some of the wafers were also measured by μ-PCD that allows the mapping of minority carrier lifetime at higher injection level ($\sim 10^{15}\,cm^{-3}$).

After illumination, the copper spot becomes visible in both SPV and μ-PCD maps. Hence, light-activated copper defects are highly recombination active at both high and low injection level. This is a different behavior compared to iron impurities. Indeed, the recombination activity of interstitial iron (Fe_i) is known to be strongly injection dependent, so that the lifetime measured after exposure to illumination (dissociation of Fe-B pairs) significantly increases at high injection and decreases at low excess carrier concentrations.[21,22] There is thus a clear advantage of using high injection (μ-PCD) for copper detection, as the effect of copper contamination can be easily separated from iron impurities. Note that in this letter, we have dissociated Fe-B pairs before any degradation experiments through an initial dark anneal step, so that the possible presence of iron contamination cannot influence our low-injection measurements.

Figure 2(a) shows a μ-PCD lifetime map after 10 min of ALID. Stronger degradation is detected in the center of the

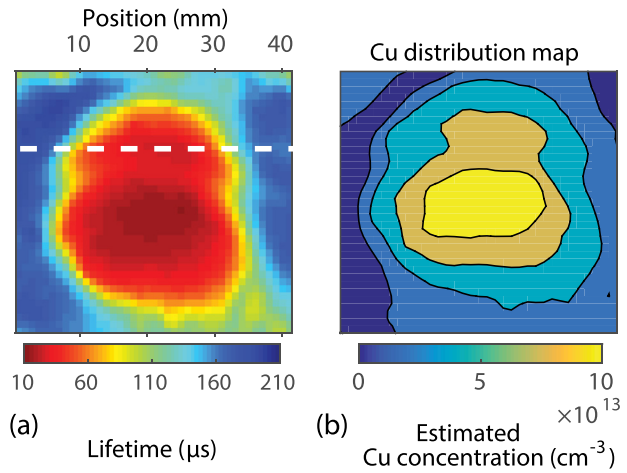

FIG. 2. (a) μ-PCD map after ALID (10 min), (b) spatial distribution map of copper calculated through Eq. (1). The dashed white line in (a) shows the line-scan position used for the data reported in Figure 3.

contaminated region, suggesting that copper tends to accumulate in the middle of the spot and its concentration progressively decreases towards the spot edges. This is in accordance with previous studies on Cu-LID, where the initial interstitial copper concentration N_{Cu} was found to be proportional to the degradation strength through the following empirical equation:[6]

$$N_{Cu} = C\left(\frac{1}{\tau_{deg}} - \frac{1}{\tau_{init}}\right)^{0.5}, \quad (1)$$

where C is a pre-factor fitted in Ref. 6 from μ-PCD lifetime results, τ_{init} is the lifetime value before degradation, and τ_{deg} represents the lifetime measured after ALID.

Figure 2(b) displays the copper concentration in each point of the copper spot shown in Fig. 2(a), obtained by inserting the μ-PCD lifetime maps before and after ALID into Eq. (1). Note that this calculation provides only an estimate of the copper concentration, as the numerical values given by Eq. (1) hold only under the conditions specified in Ref. 6. However, by combining ALID with a lifetime mapping technique, it is possible to achieve within only 10 min a qualitative copper distribution map, which allows to distinguish the different levels of contamination. Although complete degradation might not be reached within 10 min, Eq. (1) provides a reasonable estimation of Cu concentration, since, even in the most sensitive case, longer illumination time increases the estimated Cu concentration at most by a factor of 2. Therefore, it can be concluded that ALID provides a fast, non-contact, and non-destructive technique for measuring the interstitial copper concentration in silicon wafers.

Since both copper and B-O defects lead to lifetime degradation during light soaking, we want to separate the effect of the light-activated copper defects from the other metastable complexes in low-resistivity Cz-Si. Unlike Cu-related defects, it is well-known that B-O defects can be fully recovered by annealing at 200 °C in the dark, during which these complexes are thought to transform into a metastable inactive state.[23] After ALID, we thus annealed the samples at 200 °C for 3 min in the dark. To minimize the injection level dependence, the wafers were measured again at low-injection with SPV. Figure 3(a) shows the line-scan of the diffusion length map across the line-scan shown in Fig. 2(a) measured before degradation, after 10 min of ALID and a subsequent dark annealing at 200 °C. After annealing, Figure 3(a) shows a negligible lifetime increase in the middle of the copper spot, which is expected to be highly contaminated, whereas a larger but not complete recovery is detected near the edge of the copper spot. In order to determine whether this lifetime recovery is solely caused by the dissociation of B-O complexes, the experiment was repeated with an intentionally Cu-contaminated 250 μm thick, low resistivity (1.5 Ω cm) p-type FZ-Si wafer, which is free of B-O recombination due to its low oxygen concentration.

Figure 3(b) shows the results obtained in the FZ wafer, i.e., diffusion length measured before and after degradation, and the subsequent dark annealing at 200 °C across a similar line-scan of the copper spot. Surprisingly, after annealing a diffusion length increase is detected over the whole line-scan

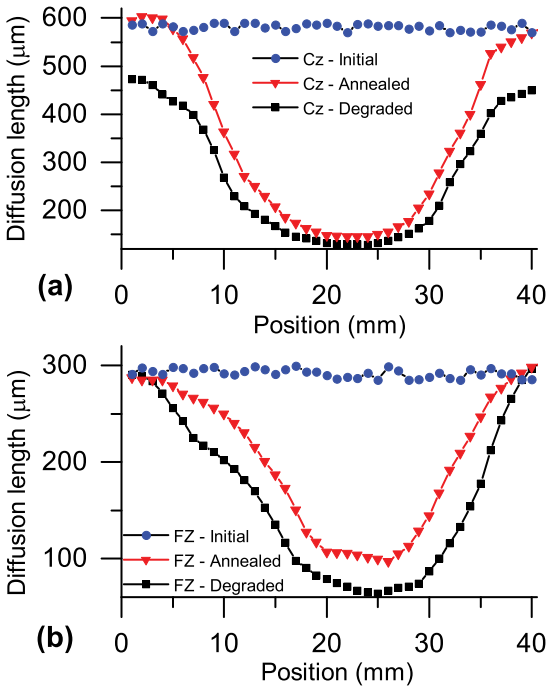

FIG. 3. Diffusion length measured with SPV before degradation (initial), after 10 min of ALID (degraded) and a subsequent 200 °C dark annealing (annealed) in spot Cu-contaminated Cz-Si (a) and FZ-Si (b).

of the copper spot. The uncontaminated reference area remains unaffected by the dark anneal, as the wafer is free of BO-LID. Any unintentional iron contamination would not affect the copper spot or the reference lifetime, since iron exists as Fe_i^+ both during degradation and annealing. Therefore, the measured lifetime recovery is clearly related to copper.

Possible copper-related reactions at 200 °C in FZ-Si include CuB dissociation, copper complex dissociation, substitutional copper (Cu_s) formation, and Cu-LID defect dissolution. CuB dissociation does not affect the lifetime, as no recombination activity has been related to CuB nor Cu_i^+. Recombination-free four-copper-atom complexes start dissociating at 150 °C[24] releasing three Cu_i^+ ions and an unknown Cu_{DLA} center,[25] which might be Cu_s.[26,27] Nevertheless, as substitutional copper is recombination active,[2] any Cu_s release would cause a lifetime decrease at 200 °C instead of the observed lifetime increase. Correspondingly, any other Cu_s formation at 200 °C would cause a further lifetime decrease, such as Cu_i^+ reaction with a vacancy,[28] a silicon self-interstitial,[29] or an oxygen-vacancy center.[30] Hence, the observed lifetime increase is concluded to be a result of Cu-LID defect dissolution. If Cu-LID were caused by recombination at substitutional copper, annealing at 200 °C might diffuse some copper from a substitutional lattice site into an interstitial, partly recovering the degraded lifetime. In case of copper precipitation being responsible for Cu-LID, the lifetime increment might be a result of precipitate dissolution, i.e., decrease of the precipitate size and/or density.

In the recent literature, only partial recovery has been observed in solar cells after LID but the reason has remained unclear.[31–33] Our results suggest that the partial recovery could be a fingerprint of copper contamination and the dark

anneal could be used to determine whether the observed degradation is caused by copper.

In this letter, we have shown that the formation kinetics of recombination active copper defects can be significantly accelerated through simultaneous annealing and illumination. A qualitative copper distribution map has been calculated through the μ-PCD lifetime values measured before and after degradation. Such method can thus be used for the rapid detection of copper contamination.

While applied to low resistivity monocrystalline Cz- and FZ-material here, this method can, in principle, be extended to quasi-mono and multicrystalline silicon. In low-resistivity Cz-silicon, however, one needs to distinguish copper-related defects from metastable BO-complexes and, for this purpose, we investigated the effect of dark annealing after degradation. Interestingly, we observed a noticeable lifetime increase in lowly Cu-contaminated wafers that cannot be solely attributed to the dissociation of BO-complex, since a similar phenomenon was observed in oxygen-free FZ-silicon. This finding led us to conclude that the observed lifetime recovery results from the dissolution of Cu-LID defects. However, since the recovery seems not to be complete in the copper contaminated regions, the dark anneal can be used to determine whether the observed degradation is caused by copper contamination.

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